

Moment Closure Schemes for Quantum Hydrodynamics

Keith H. Hughes and Steven M. Parry

School of Chemistry, Bangor University, UK

In collaboration with

Irene Burghardt, *Département de Chimie, Ecole Normale Supérieure, Paris, France*

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Overview

- Representations
- Moments from the Wigner function
- Moments from the density matrix
- Hydrodynamic equations
- Moment Closure schemes
- Maximum Entropy Method
- Hermite closure
- Applications



Mixed states

Quantum Liouville equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} \mathcal{L} \rho = -\frac{i}{\hbar} [H, \rho]$$

In coordinate x, x'

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho(x, x') &= \frac{-\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2} \right] \rho(x, x') + [V(x) - V(x')] \rho(x, x') \\ &= \frac{1}{m} \mathcal{P}' \mathcal{P} \rho(x, x') + \mathcal{V} \rho(x, x') \end{aligned}$$

where $\mathcal{P}' = \frac{\hbar}{i} \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial x'} \right)$ and $\mathcal{P} = \frac{\hbar}{2i} \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'} \right)$.

W. R. Frensley, *Rev. Mod. Phys.* **62**, 745 (1990).

In q, p phase-space

$$\rho_W(q, p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle x | \rho | x' \rangle e^{-i\frac{rp}{\hbar}} dr = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle q + \frac{r}{2} | \rho | q - \frac{r}{2} \rangle e^{-i\frac{rp}{\hbar}} dr$$

and

$$\begin{aligned}
 \frac{\partial \rho_W}{\partial t} &= -\frac{i}{\hbar} \mathcal{L}_W \rho_W = -\frac{i}{\hbar} [H e^{i\hbar\Lambda/2} \rho_W - \rho_W e^{i\hbar\Lambda/2} H] \\
 &= -\frac{p}{m} \frac{\partial}{\partial q} \rho_W + \sum_{\substack{k=1 \\ \text{odd}}}^{\infty} \frac{1}{k!} \left(\frac{\hbar}{2i}\right)^{k-1} \frac{\partial^k V}{\partial q^k} \frac{\partial^k \rho_W}{\partial p^k} \\
 \Lambda &= \frac{\overleftarrow{\partial}}{\partial q} \frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p} \frac{\overrightarrow{\partial}}{\partial q}
 \end{aligned}$$



Hydrodynamic moments

In terms of $\rho(x, x')$ the n^{th} moment

$$\langle \mathcal{P}^n \rho \rangle_q = \int_{-\infty}^{\infty} \delta(r) \mathcal{P}^n \rho(q + r/2, q - r/2) dr$$

In terms of ρ_W

$$\langle \mathcal{P}^n \rho \rangle_q = \int_{-\infty}^{\infty} p^n \rho_W(q, p, t) dp$$

Conserved quantities

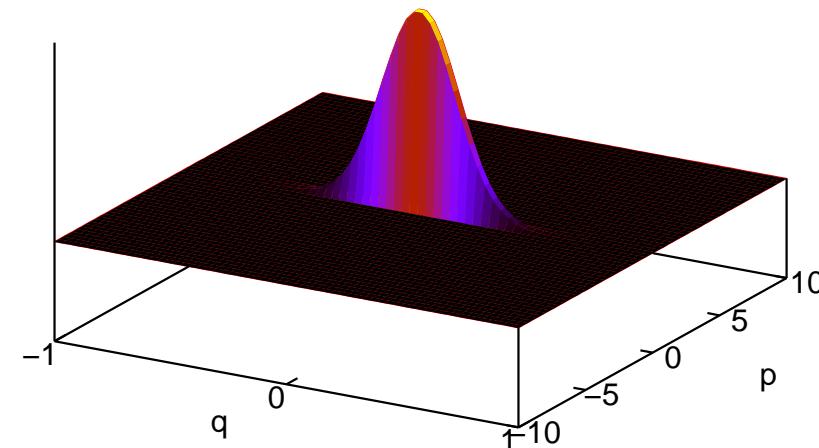
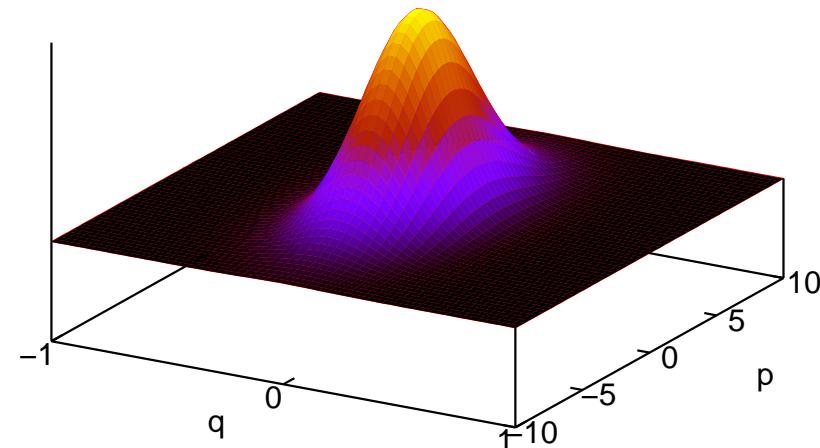
- 0th moment $\langle \rho \rangle_q \rightarrow$ local density
- 1st moment $\langle \mathcal{P} \rho \rangle_q = m \mathcal{J}(q)$. Where $\mathcal{J}(q) \rightarrow$ flux density
- 2nd moment $\langle \mathcal{P}^2 \rho \rangle_q = 2m \mathcal{T}(q)$. Where $\mathcal{T}(q) \rightarrow$ kinetic energy density.



Wigner phase space
 $\rho_W(q, p)$

\Rightarrow
 \Rightarrow

hydrodynamic phase space
 $\rho_{\text{hyd}}(q, p) = P(q)\delta[p - \bar{p}(q)]$



Equations of motion

$$\begin{aligned}
 \frac{\partial}{\partial t} \langle \rho \rangle_q &= -\frac{1}{m} \frac{\partial}{\partial q} \langle \mathcal{P} \rho \rangle_q \\
 \frac{\partial}{\partial t} \langle \mathcal{P} \rho \rangle_q &= -\frac{1}{m} \frac{\partial}{\partial q} \langle \mathcal{P}^2 \rho \rangle_q - \frac{\partial V}{\partial q} \langle \rho \rangle_q \\
 \frac{\partial}{\partial t} \langle \mathcal{P}^2 \rho \rangle_q &= -\frac{1}{m} \frac{\partial}{\partial q} \langle \mathcal{P}^3 \rho \rangle_q - 2 \frac{\partial V}{\partial q} \langle \mathcal{P} \rho \rangle_q
 \end{aligned}$$

Infinite hierarchy of equations!

Equation of motion for the n^{th} moment

$$\frac{\partial}{\partial t} \langle \mathcal{P}^n \rho \rangle_q = -\frac{1}{m} \frac{\partial}{\partial q} \langle \mathcal{P}^{n+1} \rho \rangle_q - \sum_{\substack{k=1 \\ \text{odd}}}^n \binom{n}{k} \left(\frac{\hbar}{2i}\right)^{k-1} \frac{\partial^k V}{\partial q^k} \langle \mathcal{P}^{n-k} \rho \rangle_q$$

I. Burghardt and L. S. Cederbaum, *J. Chem. Phys.*, **115**, 10303, 10312, (2001).

Generally - need a truncation scheme.
 Exceptions

- Gaussian mixed state density

$$\langle \mathcal{P}^3 \rho \rangle_q = \bar{p}^3(q) \langle \rho \rangle_q + 3\bar{p}(q) \left(\langle \mathcal{P}^2 \rho \rangle_q - \bar{p}^2(q) \langle \rho \rangle_q \right)$$

- pure states

$$\langle \mathcal{P}^2 \rho \rangle_q = -\bar{p}(q) \langle \rho \rangle_q - \frac{\hbar^2}{4} \langle \rho \rangle_q \frac{\partial^2}{\partial q^2} \ln \langle \rho \rangle_q$$

where

$$\bar{p}(q) = \frac{\langle \mathcal{P} \rho \rangle_q}{\langle \rho \rangle_q}$$

Moment Closure Schemes

Maximum Entropy Method

$$S[\rho_W] = - \int \left(\rho_W \ln \frac{\rho_W}{\rho_\beta} + \rho_\beta - \rho_W \right) dp dq$$

The ρ_W that maximizes S provides the best unbiased distribution function based on the information given - in this case the finite number of $\langle \mathcal{P} \rho \rangle_q$ that are known.

Variational problem → maximize S subject to the constraints that the lower moments are satisfied.

$$\mathcal{J}[\rho_W, \lambda] = S[\rho_W] - \int \sum_n \lambda_n(q) \left(\int p^n \rho_W dp - \langle \mathcal{P}^n \rho \rangle_q \right) dq$$

$\lambda_n(q)$ are the position q dependent Lagrange multipliers.

C. D. Levermore, *J. Stat. Phys.*, **83**, 1021, (1996)., P. Degond and C. Ringhofer, *J. Stat. Phys.*, **112** 587, (2003).



Setting

$$\delta \mathcal{J} = 0 = -\ln \frac{\rho_W}{\rho_\beta} - \sum_n \lambda_n p^n$$

The distribution function that maximizes the entropy is then given by

$$\rho_{W_A} = \rho_\beta \exp\left(-\sum_n \lambda_n(q) p^n\right)$$

$$\rho_\beta = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \exp(-\beta p^2)$$

Disadvantages:

- Determination of the Lagrange multipliers involves solving a set of n non-linear equations at all time-steps and for all values of q .
- Maximum entropy requires $\rho_{W_A} \geq 0 \forall q, p$

Alternative → linearisation of the Maximum Entropy derived ρ_{W_A} and expand in a Hermite basis.

$$\rho_{W_A} = \rho_\beta e^{-\sum_m \lambda_m(q)p^m} \simeq \rho_\beta \sum_m N_m a_m(q) H_m(p)$$



Grad-Hermite approach

The Grad-Hermite approach involves the expansion of $\rho_{\beta}^{-\frac{1}{2}} \rho_{W_A}$ in an orthonormal Hermite basis

$$\rho_{\beta}^{-\frac{1}{2}} \rho_{W_A} = \sum a_m(q) \left(\frac{\beta}{\pi} \right)^{\frac{1}{4}} \exp(-\beta p^2/2) H_m(\sqrt{\beta} p) N_m$$

where

$$\begin{aligned} a_m(q) &= \int \rho_{W_A} H_m(\sqrt{\beta} p) dp \\ &= N_m H_m(\langle \mathcal{P} \rho \rangle_q) \end{aligned}$$

$$\text{e.g. } H_3(\langle \mathcal{P} \rho \rangle_q) = 8\langle \mathcal{P}^3 \rho \rangle_q - 12\langle \mathcal{P} \rho \rangle_q$$

→

H. Grad, *Communications on Pure and Applied Mathematics*, **2**, 311, (1949).

$$\rho_{W_A} = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \exp(-\beta p^2) \sum_m N_m^2 H_m(\sqrt{\beta}p) H_m(\langle \mathcal{P}\rho \rangle_q)$$

the $(n + 1)^{\text{th}}$ moment

$$\begin{aligned}
 \langle \mathcal{P}^{n+1}\rho \rangle_q &= \int dp p^{n+1} \rho_{W_A} \\
 &= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \sum_m N_m^2 H_m(\langle \mathcal{P}\rho \rangle_q) \int p^{n+1} H_m(\sqrt{\beta}p) \exp(-\beta p^2) dp
 \end{aligned}$$

Why not take direct expansion of ρ_{W_A} ?

$$\rho_{W_A} = \sum_m a_m(q) N_m\left(\frac{\beta}{\pi}\right) H_m(\sqrt{\beta}p) \exp(-\beta p^2/2)$$

$$a_m(q) = \int \rho_{W_A} H_m(\sqrt{\beta}p) \exp(-\beta p^2/2) dp$$

$a_m(q)$ has no straightforward relation to the moments.

However, convergence to ρ_W is better.



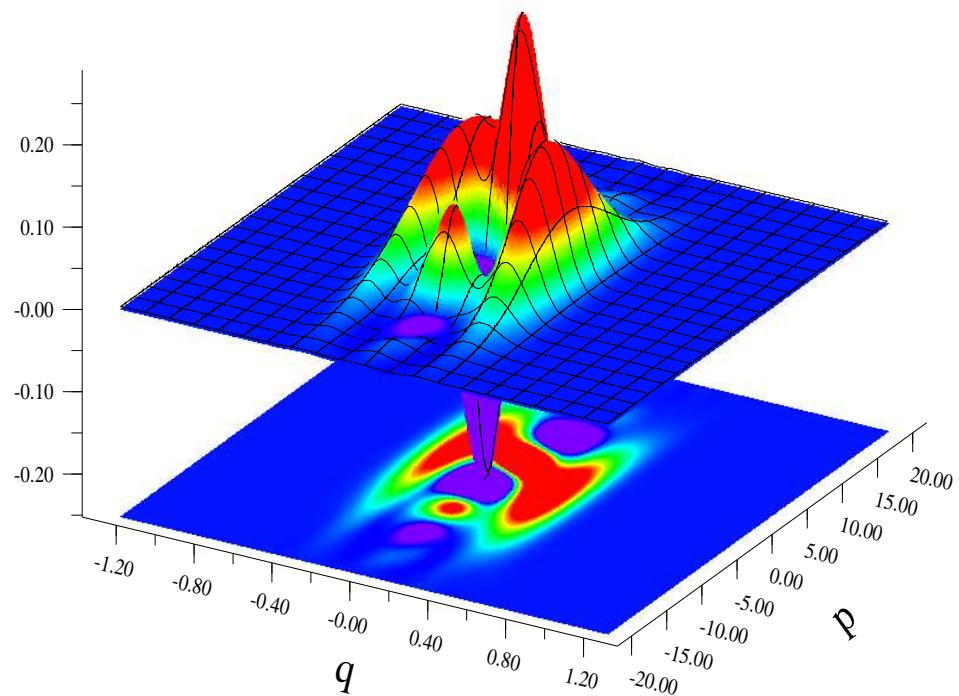
$a_m(q)$ can also be obtained by solving

$$\begin{bmatrix} h_0^0 & h_0^1 & \dots & h_0^m \\ h_1^0 & h_1^1 & \dots & h_1^m \\ \vdots & \vdots & \ddots & \vdots \\ h_n^0 & h_n^1 & \dots & h_n^m \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ \vdots \\ a_m \end{bmatrix} = \begin{bmatrix} \langle \rho \rangle_q \\ \langle \mathcal{P}\rho \rangle_q \\ \vdots \\ \langle \mathcal{P}^n \rho \rangle_q \end{bmatrix}$$
$$\mathbf{ha} = \mathbf{p}$$

$$h_n^m = \int p^n H_m(\sqrt{\beta}p) \exp(-\beta p^2/2) dp$$

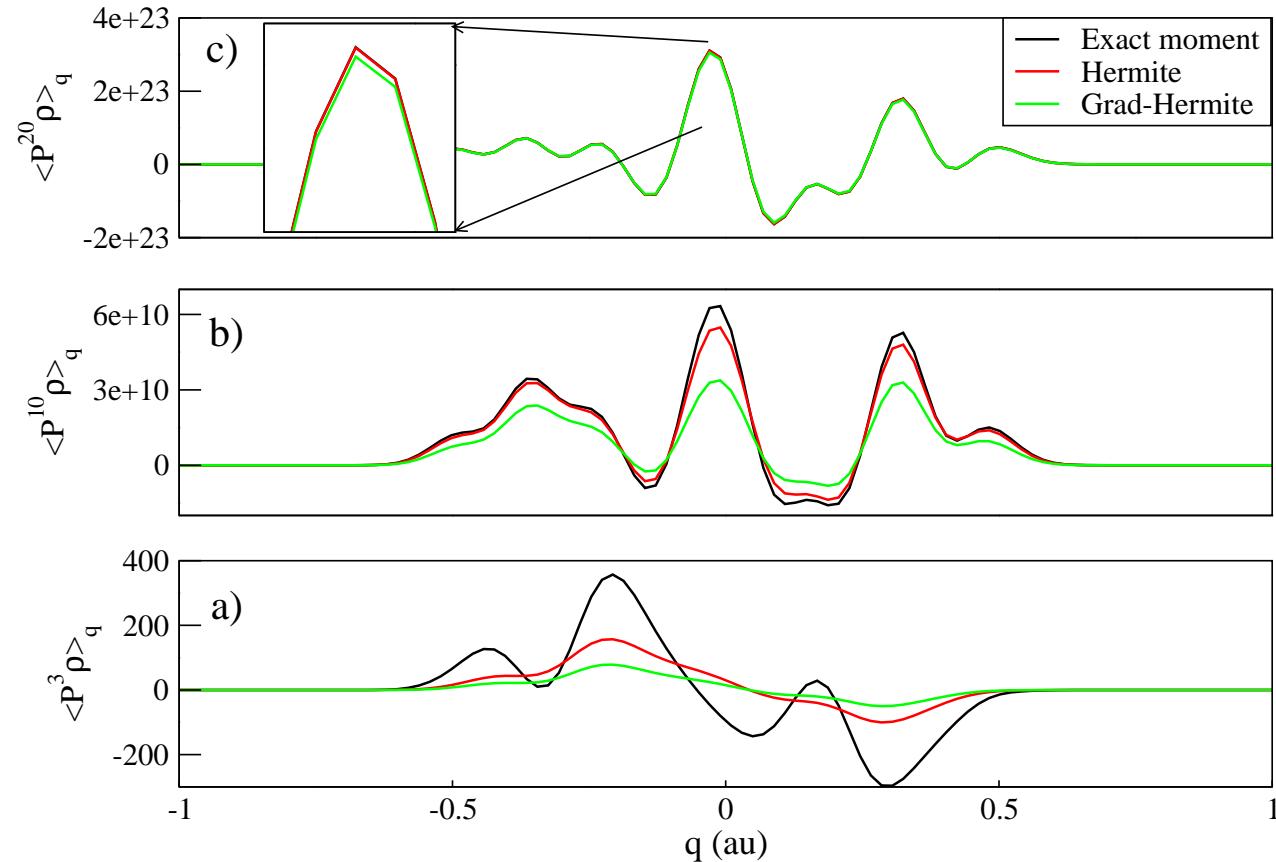


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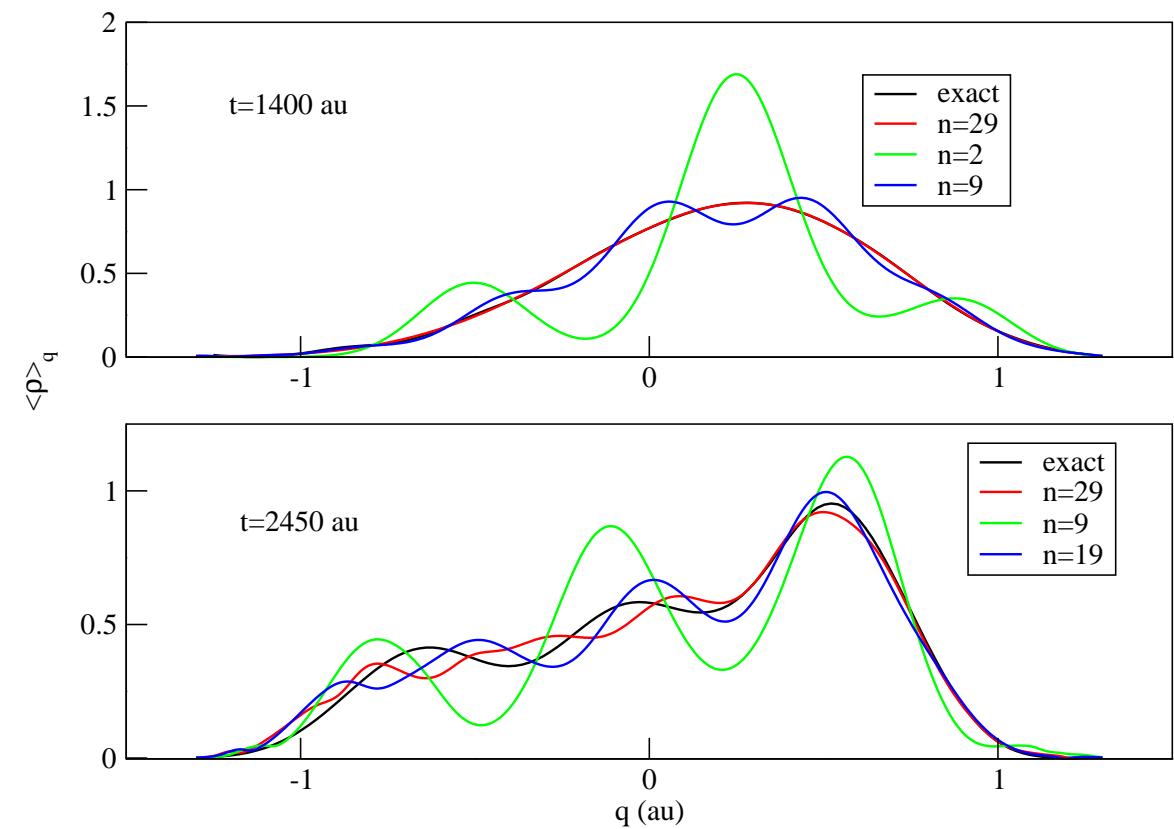
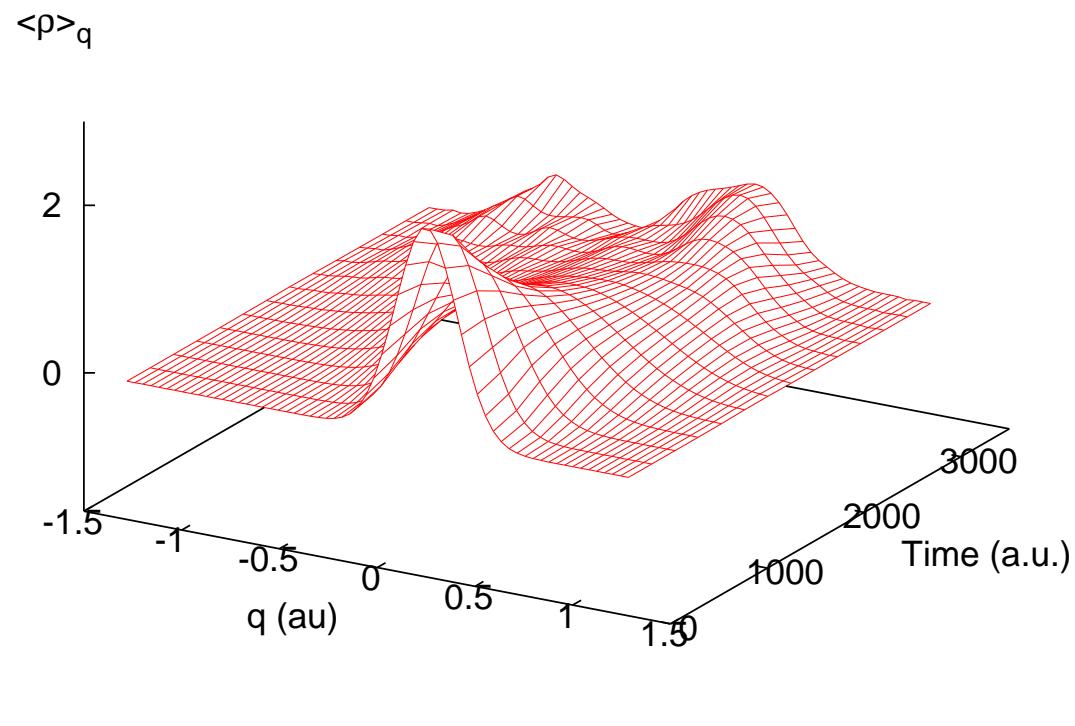


Reproduction of $\langle \mathcal{P}^{n+1} \rho \rangle_q$



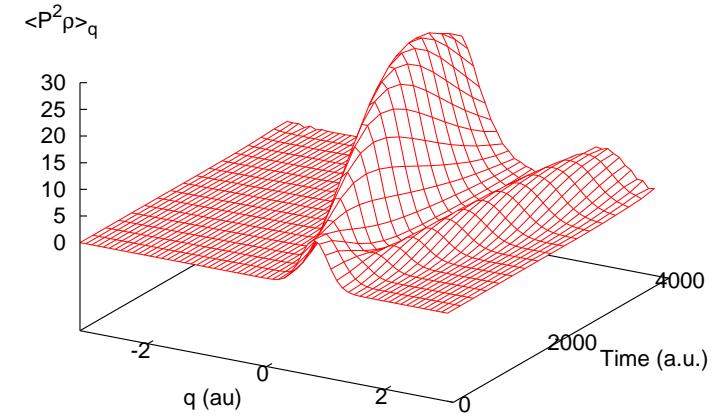
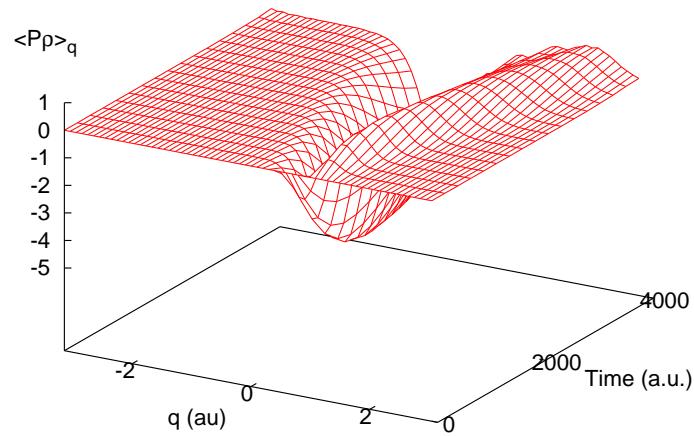
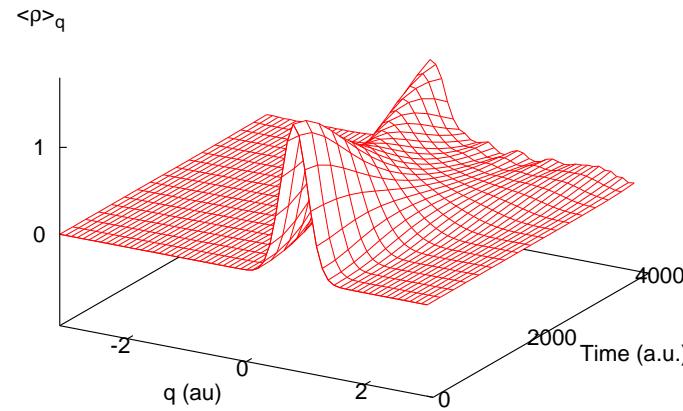


Dynamics - Quartic Oscillator V_4q^4



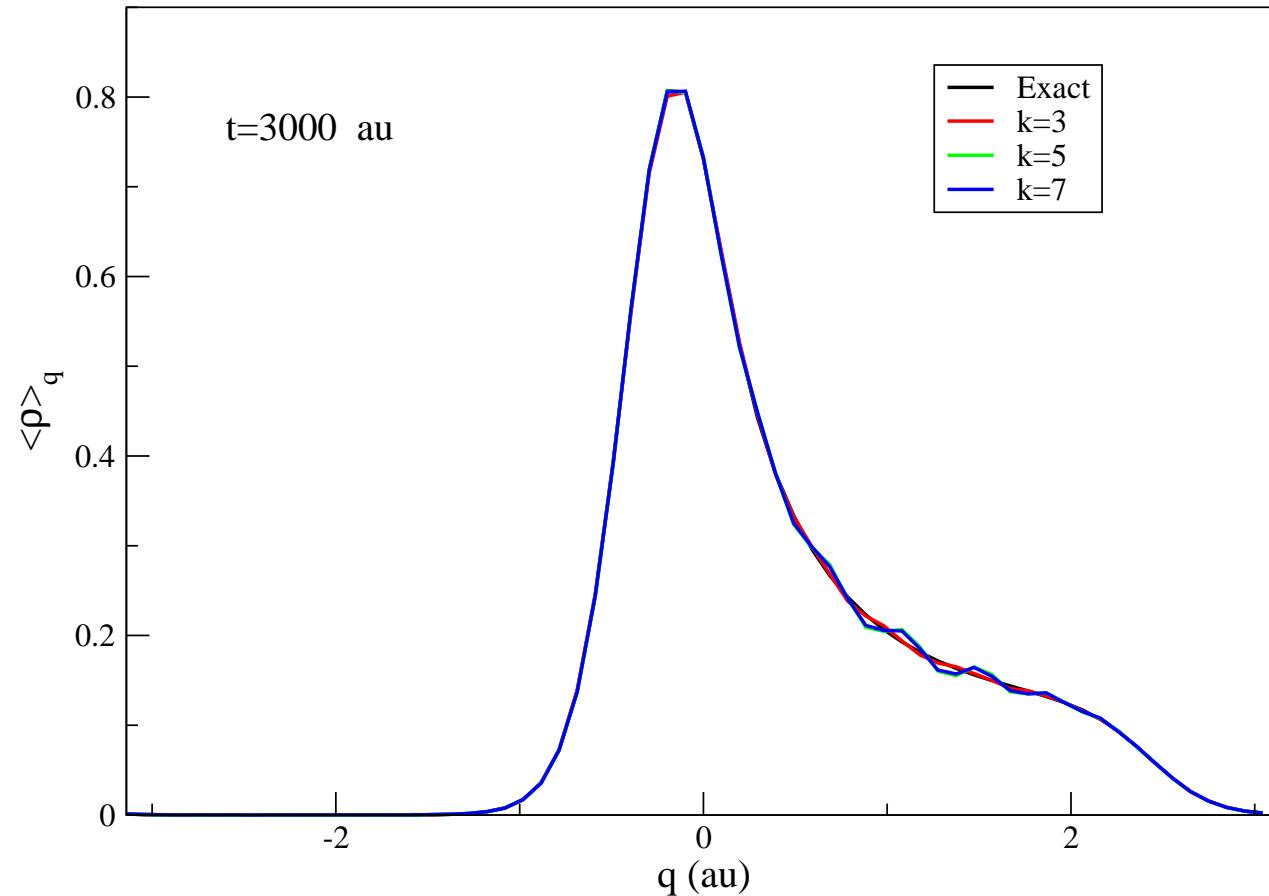


Dynamics - Periodic Potential $V_3(1 - \cos 3q)$





Influence of $\partial^k V / \partial q^k$



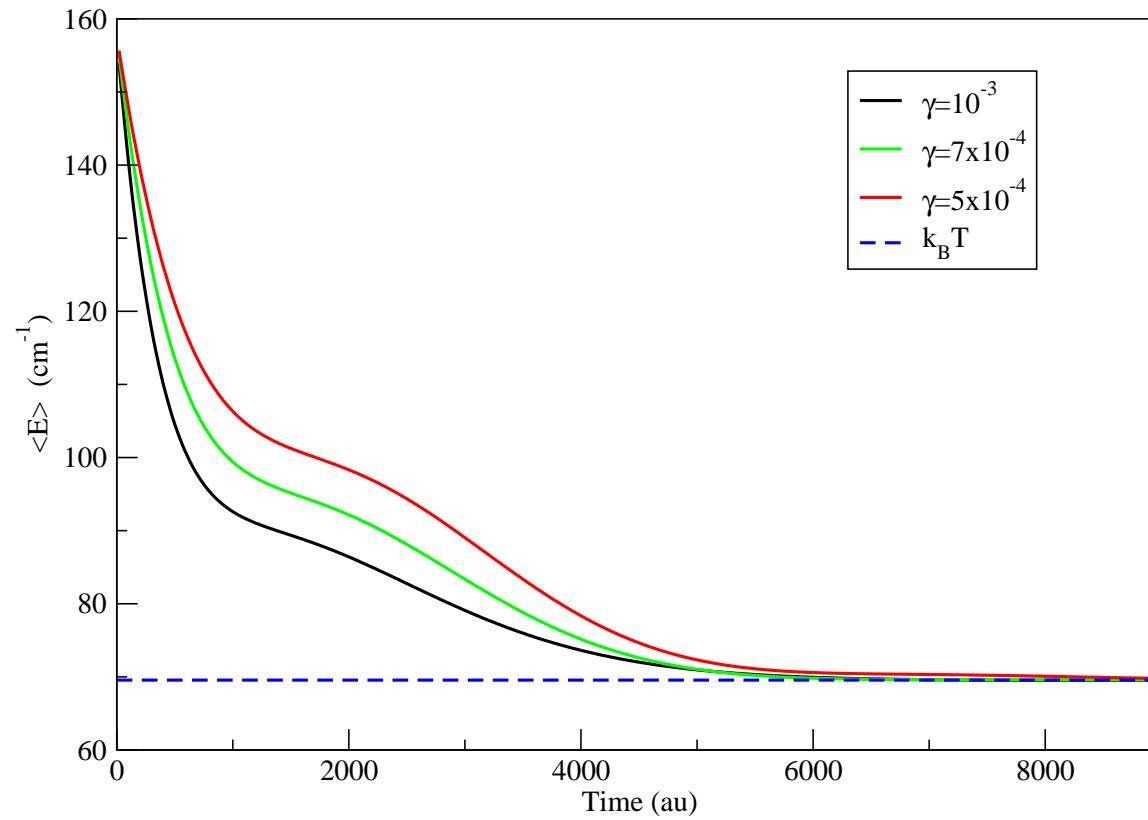


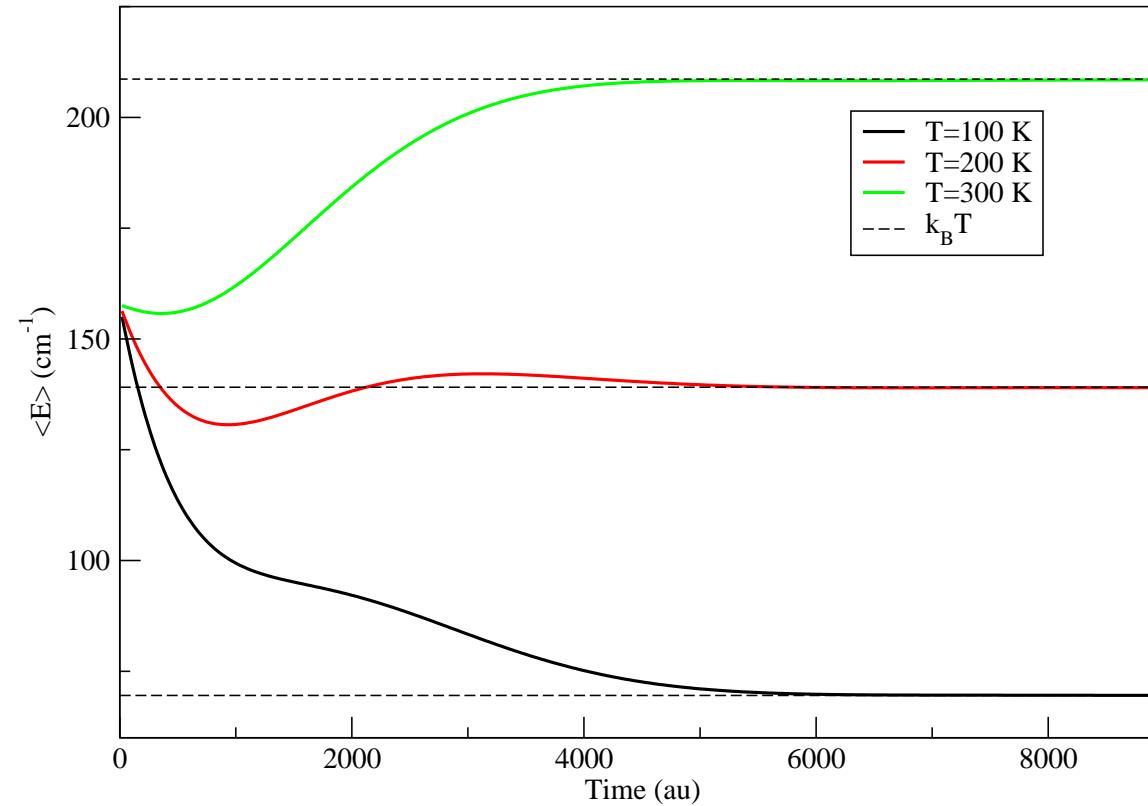
Dissipative dynamics

Caldeira-Leggett equation if hydrodynamic form

$$\begin{aligned}\frac{\partial}{\partial t} \langle \mathcal{P}^n \rho \rangle_q &= -\frac{1}{M} \frac{\partial}{\partial q} \langle \mathcal{P}^{n+1} \rho \rangle_q - \sum_{\substack{k=1 \\ \text{odd}}}^n \binom{n}{k} \left(\frac{\hbar}{2i}\right)^{k-1} \frac{\partial^k V}{\partial q^k} \langle \mathcal{P}^{n-k} \rho \rangle_q \\ &\quad - n\gamma \langle \mathcal{P}^n \rho \rangle_q + n(n-1)\gamma M k_B T \langle \mathcal{P}^{n-2} \rho \rangle_q\end{aligned}$$

I. Burghardt and K. B. Møller, *J. Chem. Phys.* **117**, 7409 (2002)





Summary

- Hermite moment closure can be applied to quantum hydrodynamics.
- Numerically appealing - no non-linear equations to solve.

Future Work

- Increase propagation time-scales.
- Implement in a Lagrangian framework.

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References:

- I. Burghardt and L. S. Cederbaum, *J. Chem. Phys.*, **115**, 10303,10312 (2001)
- I. Burghardt and K. B. Møller, *J. Chem. Phys.*, **117**, 7409 (2002)
- E. R. Bittner and J. B. Maddox, *Int. J. Quant. Chem.*, **89**, 313 (2002)
- I. Burghardt and G. Parlant, *J. Chem. Phys.*, **120**, 3055 (2004)
- I. Burghardt, K. B. Møller, G. Parlant, L. S. Cederbaum and E. R. Bittner *Int. J. Quant. Chem.*, **100**, 1153 (2004)
- I. Burghardt, *J. Chem. Phys.*, **122**, 094013 (2005)
- I. Burghardt, K. B. Møller and K. H Hughes, *Quantum Dynamics of Complex Molecular Systems*, Springer (2007)
- K. H. Hughes, S. M. Parry, G. Parlant and I. Burghardt, *J. Phys. Chem. A*, **111**, 10269, (2007).